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Extreme drought decouples silicon and carbon geochemical linkages in lakes

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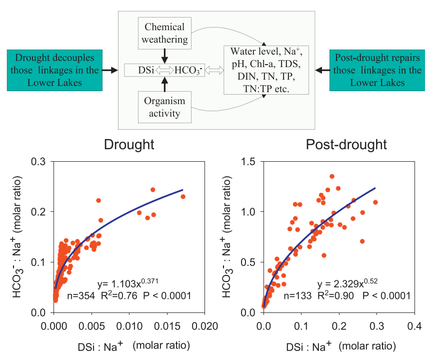
HIGHLIGHTS

- DSi concentration is lower but HCO_3^- concentration is higher in drought period.
- DSi:Na^+ markedly correlated with HCO_3^-:Na^+ in both drought and post-drought periods.
- DSi:HCO_3^- has weaker correlations with environmental factors in the drought period.
- DSi:HCO_3^- is predicted by TN in drought but by pH, TN and TP in post-drought period.
- Drought decouples the silicon and carbon geochemical linkages in the Lower Lakes.

GRAPHICAL ABSTRACT



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ABSTRACT

Silicon and carbon geochemical linkages were usually regulated by chemical weathering and organism activity, but had not been investigated under the drought condition, and the magnitude and extent of drought effects remain poorly understood. We collected a comprehensive data set from a total of 13 sampling sites covering the main water body of the largest freshwater lake system in Australia, the Lower Lakes. Changes to water quality during drought (April 2008–September 2010) and post-drought (October 2010–October 2013) were compared to reveal the effects of drought on dissolved silica (DSi) and bicarbonate (HCO_3^-) and other environmental factors, including sodium (Na^+), pH, electrical conductivity (EC), chlorophyll *a* (Chl-*a*), total dissolved solids (TDS), dissolved inorganic nitrogen (DIN), total nitrogen (TN), total phosphorus (TP) and water levels. Among the key observations, concentrations of DSi and DIN were markedly lower in drought than in post-drought period while pH, EC and concentrations of HCO_3^-, Na^+, Chl-*a*, TDS, TN, TP and the ratio TN:TP had inverse trends. Stoichiometric ratios of DSi:HCO_3^-, DSi:Na^+ and HCO_3^-:Na^+ were significantly lower in the drought period. DSi exhibited significantly negative relationships with HCO_3^-, and DSi:Na^+ was strongly correlated with HCO_3^-:Na^+ in both drought and post-drought periods. The backward stepwise regression analysis that could avoid multicollinearity suggested that DSi:HCO_3^- ratio in drought period had significant relationships with fewer variables when compared to the post-drought, and was better predictable using nutrient variables during post-drought. Our results highlight the drought effects on variations of water constituents and point to the decoupling of silicon and carbon geochemical linkages in the Lower Lakes under drought conditions.

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1. Introduction

Dissolved silica (DSi) and bicarbonate (HCO_3^-) enter aquatic ecosystems (Wang et al., 2016) at a stoichiometric ratio when silicate minerals chemically weather (Gaillardet et al., 1999; Beaulieu et al., 2010). In lakes, the planktonic diatoms utilise dissolved silica (DSi) for building their frustules and carbon (C) to form organic molecules (Brzezinski, 1985; Wang et al., 2013), indicating that diatom elemental stoichiometry links the silicon and carbon geochemical cycles. The water ratio of DSi:HCO_3^- thus will be affected by diatom uptake which could be reflected by chlorophyll *a* (Chl-*a*) and impacted by environmental factors such as pH, electrical conductivity (EC), total dissolved solids (TDS), total nitrogen (TN), total phosphorus (TP) (Chen et al., 2009; Håkanson and Boulion, 2003; Kalin et al., 2001; Phlips et al., 1995). The DSi:HCO_3^- stoichiometry in return links with ecological processes (Sicko-Goad et al., 1984). This is significant because DSi:HCO_3^- ratio can reflect phytoplankton habitat and reliant diatom activity in lakes (Assmy et al., 2013; Hutchins and Bruland, 1998; Macuiane et al., 2011). Wang et al. (2016) complied a series of data about silica and carbon from lakes in the United States of America and the United kingdom, and showed that the sign of correlation between HCO_3^-:Na^+ and DSi:Na^+ were opposite in the English Lake district and the American Lakes, while the DSi:HCO_3^- ratios were both negatively correlated with Chl-*a*. However, there still have been few studies focus on the correlations between water quality factors and DSi:HCO_3^- ratio in lakes, particularly lakes under the effects of extreme drought.

Given the anticipated increasing frequency and intensity of drought under anthropogenic activity and changing climate, DSi:HCO_3^- stoichiometry could play an expanded role in linking chemical weathering and diatom productivity (Wang et al., 2016), providing a new perspective for biogeochemical cycles of nutrients and water quality management in lakes.

Drought significantly destabilizes the aquatic ecosystem by altering the water level, salinity, acidification, temperature and eutrophication of lakes (Yan et al., 1996; Lathrop, 2007; Jirsa et al., 2013), This is likely because drought not only shifts the physical factors (e.g. residence time, flushing/outflows and evapoconcentration) (Flanagan et al., 2009; Olds et al., 2011), but also changes the biochemical processes (e.g. photosynthesis, respiration and reaeration) in lakes (Baldwin et al., 2008; Aldridge et al., 2011; García-Jurado et al., 2012). Moreover, decline of water level in the drought period may lead to exposure of sulfidic benthic sediments and the formation of acid sulfate soils, and the acidification of surface water occurs when re-inundation (Mosley et al., 2014b). Previous studies have investigated the drought effects on water quality of lakes (e.g. water level, pH, EC, nutrients and Chl-*a*) (Mosley, 2015 and references therein). However, there is limited information on the drought effects on characterization of DSi:HCO_3^- ratio and the correlations between stoichiometric DSi:HCO_3^- and other determinants in lakes.

Over the past decade, the Murray-Darling Basin (MDB), Australia's largest arid to semi-arid river system in Australia, was gripped by a severe drought due to rainfall reductions and water over allocation that resulted in a prolonged decline in water levels of the Lower Lakes (Lakes Alexandrina and Albert) at the downstream mouth of river systems in MDB (Mosley et al., 2012). Under drought conditions the Lower Lakes experienced increased salinity (Mosley et al., 2012), water acidification (Mosley et al., 2014a, b), and eutrophication (Li et al., 2017), and an altered atmospheric CO_2 cycle (from sink to source) (Li et al., 2016). With such significant changes to water quality during drought, it is reasonable to anticipate systematic shifts in biogeochemical processes and stoichiometry of nutrients, such as stoichiometric DSi:HCO_3^- as a consequence of its influence on diatom algae activities. This encourages a further study on silicon and carbon geochemical linkages in the Lower Lakes particularly in relation to the drought.

Our objectives in this study are therefore to (1) quantify the drought effects on the DSi:HCO_3^- ratio and other key environmental factors, and (2) identify the most important factors governing water variables particularly DSi, HCO_3^- and DSi:HCO_3^- stoichiometric ratio in the Lower Lakes. We hypothesize that drought decreases the DSi:HCO_3^- ratio and decouples the correlations between DSi:HCO_3^- stoichiometric ratio and other environmental properties.

2. Methodology

2.1. Study area

A detailed description of the Lower Lakes (Lakes Alexandrina and Albert) (35°25′ S, 139°07′E) has been given by Li et al. (2016, 2017). Briefly, the Lower Lakes are situated at the mouth of the Murray River and are the major water storage for the lowest extent of the vast Murray-Darling Basin (MDB) (Fig. 1). The dominant climate is subtropical to semi-arid with a distinct seasonality of temperature and rainfall. The mean monthly temperature varies between 10.1 °C (July) and 20.2 °C (January) (Li et al., 2016). Average annual rainfall is 423 $\pm$ 7.6 mm with large inter and intra-annual fluctuation with about 75% occurring between April and September. Mean monthly evapotranspiration (ET) ranges from 34.2 (June) to 175.4 (January) mm with an annual average of 1212.7 $\pm$ 113.9 mm/y, 2.9 times higher than annual mean rainfall (Li et al., 2016). The Lower Lakes totally cover an area of 820 km^2. Thereinto, Lake Alexandrina is the larger one and has a surface area of 650 km^2 with a volume of approximately 1585 Mm^3 and a mean depth of 2.4 m (maximum depth is about 4.1 m), while the smaller one, Lake Albert, has a surface area of 170 km^2 with a volume of approximately 264 Mm^3 and a mean depth of 1.5 m (maximum depth is about 2.3 m) (Mosley et al., 2012). A narrow channel connects the Lake Alexandrina and Lake Albert. Whereas, Lake Alexandrina had a reduction of 14% in surface area, 43% volume and 33% mean water depth, and Lake Albert had a decline of 15% in surface area, 57% in mean depth and 47% volume (Mosley et al., 2012) respectively during the drought period (April 2008–September 2010) (Mosley et al., 2012). Thereinto, from March 2008, the water level of Lake Alexandrina fell below −0.2 m AHD and resulted in a hydrological disconnection in Lakes Alexandrina and Albert. Thus, the South Australian government took measures to manage the smaller and shallower Lake Albert through constructing the temporary bund wall and launching pumping to replenishment. A quick lake refill occurred from February to September 2010 due to floods caused by major rainfall events in the MDB. It was in the October 2010 that Lower lakes entered the post-drought period (Li et al., 2017).

The Lower Lakes are characteristically eutrophic and highly turbid (Cook et al., 2010; Mosley et al., 2012). A barrage constructed >80 years ago prevents seawater intrusion to Lake Alexandrina and regulates water yield for irrigation and domestic supply for consumption in the local region (Li et al., 2016). Historically, large volumes of drainage water containing nutrients and pathogens from upstream flood-irrigated agricultural land have been returned to the Murray River (Murray and Philcox, 1995), which affected the water quality of Lower Lakes as the Murray River supplies main water inflow for the Lower Lakes (Mosley et al., 2014b). Most of the Lakes' upper-lands had been improved recently by constructing water delivery infrastructures to minimize pollutants in the drainage channels (Mosley and Fleming, 2010). Water level of the Lower Lakes is sensitive to the flow allocation from the highly regulated Murray River system and/or evaporation. Local rainfall does not provide enough water supply for the Lower Lakes, as majority of the supply is governed by the broader MDB. Thus, a large area of exposure of sulfidic benthic sediments and the formation of acid sulfate soils increased in drought period, resulting in acidification of surface water of the Lower Lakes (Mosley et al., 2014b). The hydrological drought disruption was clear and a source of grave concern to authorities, communities and businesses in the region.

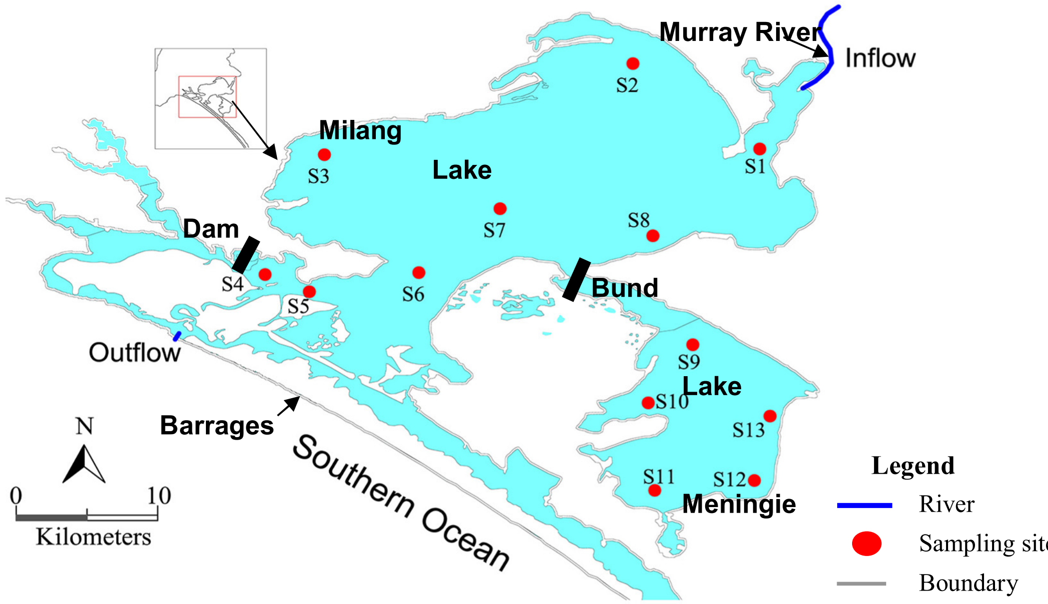

Fig. 1. Sampling sites in the Lower Lakes (Lake Alexandrina: S1 Opening, S2 Top, S3 Milang, S4 Clayton, S5 Island, S6 Point Mcleay, S7 Middle, S8 Poltalloch, S9 Opening, S10 Campell park, S11 South west, S12 Meningie, S13 Water level recorder; a total of 8 sites in Lake Alexandrina and 6 sites in Lake Albert).

2.2. Data sources and analysis

Long-term water environmental data of the Lower Lakes was collected from the South Australian Environmental Protection Authority (SAEPA) water quality database (http://www.epa.sa.gov.au/environmental_info/water_quality/lower_lakes_monitoring/reports_and_data). Each site had either fortnightly, or monthly data, between April 2008 and December 2012. Three sites had data extending to October 2013 (i.e. Opening, Meningie and Water level recorder in Lake Albert). As long-term monitoring sites, Milang and Meningie stations recorded the daily variations of water levels of Lake Alexandrina and Lake Albert. For this study, a total of 13 sites were used to assess silicon and carbon linkages across the Lakes, 8 sites in Lake Alexandrina and 6 sites in Lake Albert (Fig. 1). The selection of these sampling sites was based on their spatial representation of the main water body and completeness of datasets in term of the number and consistency of determinants measured over the period of interest.

Water samples were collected in accordance with standard practice (APHA, 2005, 2012) for an open water body and transported in ice-filled cooler boxes to the Australian Water Quality Centre (AWQC) laboratory in Adelaide and then stored at 4 °C. Strict sample analyses following the standard methods were performed. Specifically, duplicate grab samples were collected at a depth of approximately 10–30 cm using acid washed polypropylene bottles. The surface water temperature, pH, electrical conductivity (EC) and chlorophyll *a* (Chl-*a*) were determined in the field using calibrated electrodes linked to a TPS90-FLMV multi-parameter meter. Dissolved and total nutrients samples (nitrate, nitrite, ammonia, total nitrogen, TN; total phosphorus TP) were analyzed as per standard colorimetric methods (APHA, 2005). Dissolved silica (DSi) and sodium (Na^+) were analyzed by ICP-OES (Inductively Coupled Plasma-Optical Emission Spectrometry). Alkalinity was manually titrated in situ with HCl, and thus bicarbonate (HCO_3^-) was calculated based on temperature, pH and alkalinity. Total dissolved solids (TDS) was measured by oven-dried at 105 °C. The water levels in Milang and Meningie stations were also collected. Majority of factors were expressed in $\mu mol \cdot L^{-1}$, except pH, EC ($\mu S \cdot cm^{-1}$), chlorophyll *a* ($\mu g \cdot L^{-1}$), TDS ($mg \cdot L^{-1}$) and water level (m Australian Height Datum). The basic statistics for the periods of drought (April 2008–September 2010) and post-drought (October 2010–October 2013) are summarized in Table 1. It was noted that the HCO_3^- could account for almost all of the alkalinity (Li et al., 2016) in both drought period and post-drought period, this was supported by the pH values ranged from 7.8 to 9.00 with the average 8.54 in the drought period, and varied between 7.4 and 8.8 with the average 8.3 in the post-drought period (Table 1), suggesting that monovalent bicarbonate was the dominant species of dissolved inorganic carbon in the Lower Lakes during the study period, thus we assumed that HCO_3^- could represent the changes of total carbonates in this study.

2.3. Statistical analysis

One-sample Kolmogorov-Smirnov test was used to evaluate the normal distribution of data and the log-transformation was performed when the data was not normally distributed for robust statistical analysis. Mann Whitney *U* test was employed to uncover the drought effects on selected variables. Pearson correlation analysis was implemented to underscore the relationships among variables, and simple regression method was applied to coordinate the correlations between DSi:HCO_3^- and other influence factors. Principal component analysis (PCA) was carried out to identify the most important variables for determining the influence sources in the Lower Lakes after the Kaiser-Meyer-Olkin (KMO) and Bartlett's test was satisfactory. The backward stepwise regression analysis (BSRA) was lastly adopted to unravel the closest independent variables with dependent variable DSi:HCO_3^- in terms of above analyzed results. BSRA is an extension of linear regression model. When it is performed, all potential independent variables are included in a model and then gradually eliminated to a minimum variable set, resulting in the maximum adjusted determination coefficient and the minimum mean squared deviation from the regression model (Kolasa-Wiecek, 2015). Statistical significance in this study was specified at $P < 0.05$. Majority of statistical analyses were conducted using SPSS 18.0, while the BSRA was performed using Statistica 6.0. Figures except for Fig. 1 were generated by SigmaPlot 12.5 (Figs. 2 and 3) and Statistica 6.0 (Fig. 4).

Table 1
Statistics and Mann-Whitney *U* tests of silicon, carbon and selected variables during drought (Apr. 2008–Sep. 2010) and post-drought (Oct. 2010–Oct. 2013) in the Lower Lakes.

Variable	Drought					Post-drought					Significant level	
	n	Min.	Max.	Mean	S.D.	n	Min.	Max.	Mean	S.D.	Mann-Whitney *U*	*P*
DSi (μmol·L^{-1})	354	35.71	107.14	42.17	16.84	137	35.71	428.57	171.01	87.10	1516.5	0.000
HCO_3^- (μmol·L^{-1})	354	1344.00	6558.70	3996.61	934.26	137	535.60	4672.70	2608.01	1317.95	9945.5	0.000
Na^+ (μmol·L^{-1})	354	1543.50	191,739.10	65,001.41	40,281.05	133	956.50	77,826.10	22,446.55	23,372.02	8849	0.000
DSi:Na^+ (molar ratio)	354	0.0002	0.02	0.0013	0.00	133	0.001	0.30	0.06	0.07	2135	0.000
HCO_3^-:Na^+ (molar ratio)	354	0.02	2.86	0.09	0.15	133	0.06	1.35	0.41	0.37	7802	0.000
DSi:HCO_3^- (molar ratio)	354	0.01	0.07	0.01	0.01	137	0.01	0.37	0.09	0.07	1410	0.000
EC (μS·cm^{-1})	354	910.00	22,400.00	8497.15	4751.33	136	192.00	10,200.00	3318.84	3159.61	9782.5	0.000
pH	354	7.80	9.00	8.54	0.21	137	7.40	8.80	8.30	0.35	15,042.5	0.000
Chl-*a* (μg·L^{-1})	296	16.40	225.00	78.50	34.50	105	14.70	114.00	53.99	19.56	8868	0.000
Water level (m AHD)[a]	61	−0.88	0.75	−0.35	0.29	21	0.58	0.83	0.70	0.06	27.5	0.000
DIN (μmol·L^{-1})	174	0.20	99.00	3.23	9.20	137	0.40	30.40	3.75	5.46	7120	0.000
TDS (mg·L^{-1})	354	542.40	13,931.00	5103.77	2989.39	137	115.20	6128.90	1958.99	1885.00	9838	0.000
TN (μmol·L^{-1})	344	34.30	502.90	227.81	85.56	132	25.00	239.30	131.99	43.11	7418.5	0.000
TP (μmol·L^{-1})	345	0.50	19.30	5.75	2.39	133	1.70	9.30	5.32	1.68	21,131	0.181
TN:TP (molar ratio)	344	13.10	189.29	42.53	18.51	132	10.87	70.61	26.92	11.98	9350.5	0.000

[a] Water levels were obtained from Milang (Lake Alexandrina) and Meningie (Lake Albert), respectively.

3. Results

3.1. Variations of water level, silicon, carbon and sodium in the Lower Lakes

Water levels at Milang and Meningie monitoring locations and the average concentrations of DSi, HCO_3^- and Na^+ in the Lower Lakes were significantly different between the drought and post-drought period ($P < 0.01$) (Table 1). The changes of water level, silicon, carbon and sodium with time at Meningie monitoring locations as example were showed in Fig. S1. Water level of Milang and Meningie was 1.5-fold lower on average in the drought period. DSi concentration was 75.3% lower during drought while HCO_3^- and Na^+ were 53.2% and 189.6% higher during drought (Table 1). Stoichiometric ratios of DSi:Na^+, HCO_3^-:Na^+ and DSi:HCO_3^- were also obviously different between drought period and post-drought period (Table 1).

Sodium (Na)-normalized DSi and HCO_3^- were used to evaluate the further relationships between DSi and HCO_3^- concentrations, to eliminate the influences on DSi and HCO_3^- concentrations from heterogeneity in factors such as land cover, runoff and evaporation in the drought and post-drought periods (Wang et al., 2016). DSi:Na^+ and HCO_3^-:Na^+ in both drought and post-drought periods showed a strong positive power correlation ($P < 0.0001$), but it was closer in the post-drought ($R^2 = 0.90$) than that in the drought period ($R^2 = 0.76$) (Table S1, Fig. 2).

3.2. Variations of analytes in the Lower Lakes

A majority of analytes in the Lower Lakes showed significant differences between drought and post-drought period ($P < 0.01$). The exception was TP ($P > 0.05$) (Table 1). Specifically, EC, pH and concentrations of Chl-*a*, TDS and TN were 156%, 2.9%, 45.4%, 160.5% and 72.6% higher during the drought period (Table 1). The stoichiometric ratio of TN:TP was 58% higher during drought than that during the post-drought period (Table 1). In contrast, DIN concentration was 13.9% lower in the drought than that in the post-drought period (Table 1).

3.3. Relationships between water level and analytes in the Lower Lakes

Water level had a clear relationship with analytes in the Lower Lakes across the drought and post-drought period (Table S1). Particularly, for the drought period, DSi concentration was significantly negatively correlated with EC, pH, Chl-*a*, TDS, TN, TP and TN:TP, and significantly positively correlated with water level and DIN, while HCO_3^- concentration was significantly positively correlated with EC, Chl-*a*, TDS, TN, TP and TN:TP, and was not significantly correlated with pH, water level and DIN (Table S1). Regression analysis showed that DSi:HCO_3^- stoichiometry was significantly negatively correlated with EC, TDS, Chl-*a*, TN, TP and TN:TP (Fig. 3). For the post-drought period, DSi concentration exhibited significantly negative correlations with EC, pH, TDS and TN:TP and positive correlation with TP, but insignificant correlations with Chl-*a*, water level, DIN and TN, while HCO_3^- concentration presented significantly positive correlations with EC, pH, TDS, TN and TN:TP, and negative correlations with DIN and TP, but insignificant correlations with Chl-*a* and water level (Table S1). Similarly, regression analysis indicated that DSi:HCO_3^- ratio had significantly negative correlations with EC, TDS, TN and TN:TP, and had significantly positive relationships with TP (Fig. 3). Overall, the correlations were closer during post-drought than those during drought period (Table S1; Fig. 3).

3.4. Variable sources in the Lower Lakes

PCA identified three important factors during the drought period in the Lower Lakes (Table 2). Those factors explained a total of 84.2% of the total variance; the first factor accounted for 55% of variance and significantly comprised DSi, HCO_3^-, Na^+, DSi:Na^+, HCO_3^-:Na^+, DSi:HCO_3^-, EC, water level, TDS, TN and TN:TP, the second factor deciphered 17.6% of variance and largely consisted of water level, DIN, TP and TN:TP, and the third factor interpreted 11.6% of variance and mainly consisted of pH and Chl-*a* (Table 2). Similarly, three factors explaining 83.2% of the total variance were also obtained in the post-drought period (Table 2). The first factor captured 54.9% of the total variance and remarkably correlated with DSi, HCO_3^-, Na^+, DSi:Na^+, HCO_3^-:Na^+, DSi:HCO_3^-, EC, pH, TDS, TP and TN:TP; the second factor accounted for 18.6% of the total variance and showed marked correlations with DSi, Chl-*a*, TN and TP, and the third factor explained 9.8% of the total variance and had elevated loadings of water level and DIN (Table 2). The first factor generally represented the chemical weathering in the catchment and the latter two factors were linked with anthropogenic pollutions from the upper reaches of the Lower Lakes for both drought and post-drought periods.

3.5. Factors influencing DSi:HCO_3^- stoichiometries in the Lower Lakes

BSRA was used to discern the most significantly independent variables related to dependent DSi:HCO_3^- considering the multicollinearity which was present among the independent variables (Kolasa-Wiecek, 2015) (Table S1). Given that the larger values of loadings corresponded to variables that contributed relatively more information to the total variance (Zhang et al., 2017) (Table 2), we selected the independent variables for drought (i.e. EC, Chl-*a*, TDS, TN, TP and TN:TP) and post-drought (i.e. EC, pH, Chl-*a*, water level, TDS, TN, TP and TN:TP) to predict the variations of dependent variable DSi:HCO_3^-. The BSRA produced the

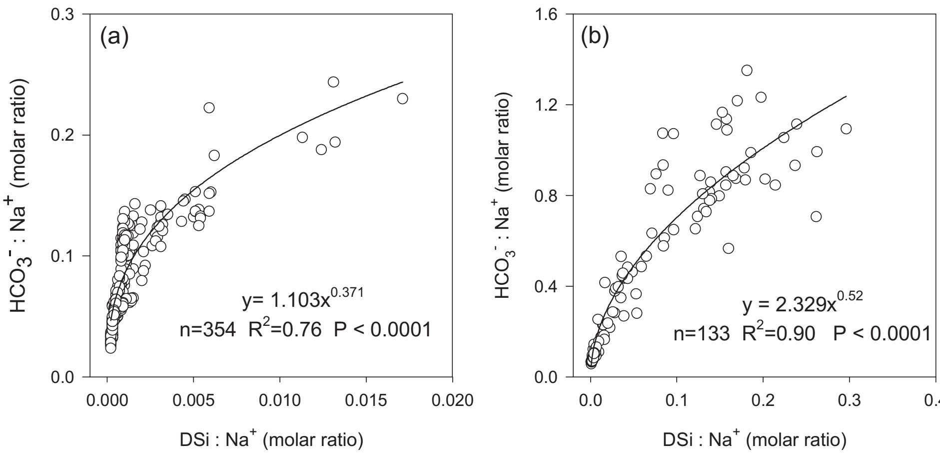

Fig. 2. Relationships between Na-normalized DSi and Na-normalized HCO_3^- during the period of drought (a) and post-drought (b) in the Lower Lakes, respectively.

following relationships for drought (Eq. (1)) and post-drought period (Eq. (2)):

$$\mathrm{DSi}:\mathrm{HCO}^-_{3(\mathrm{drought})}=0.021-3.71\times10^{-5}\mathrm{TN}\ \left(n=344,R^2=0.16,P{<}0.0001\right) \quad (1)$$

$$\mathrm{DSi}:\mathrm{HCO}^-_{3(\mathrm{post-drought})}=0.496-5.6\times10^{-2}\mathrm{pH}-1\times10^{-3}\mathrm{TN}+2.5\times10^{-2}\mathrm{TP}\ \left(n=131,R^2=0.63,P{<}0.0001\right) \quad (2)$$

where $\mathrm{DSi}:\mathrm{HCO}^-_{3(\mathrm{drought})}$ and $\mathrm{DSi}:\mathrm{HCO}^-_{3(\mathrm{post-drought})}$ are the molar ratios in the drought and post-drought period, pH is dimensionless, and TN and TP are in $\mu\mathrm{mol}\cdot\mathrm{L}^{-1}$ units.

Eqs. (1) and (2) indicated that TN was more closely related to DSi:HCO_3^- in the drought, and pH, TN and TP were most closely associated with DSi:HCO_3^- in the post-drought (Table S2). Further, as contained more independent variables, the regression equation captured more information of DSi:HCO_3^- as a dependent variable in the post-drought period than that in the drought period (Table S2, Fig. 4), indicating that drought has decoupled the correlations between DSi:HCO_3^- and other lake indices.

4. Discussion

The major determinants (HCO_3^-, Na^+, EC, pH, Chl-*a*, TDS, TN, TP) largely increased during the drought period (Table 1). The increases in the concentrations of dissolved materials are mainly due to reduction

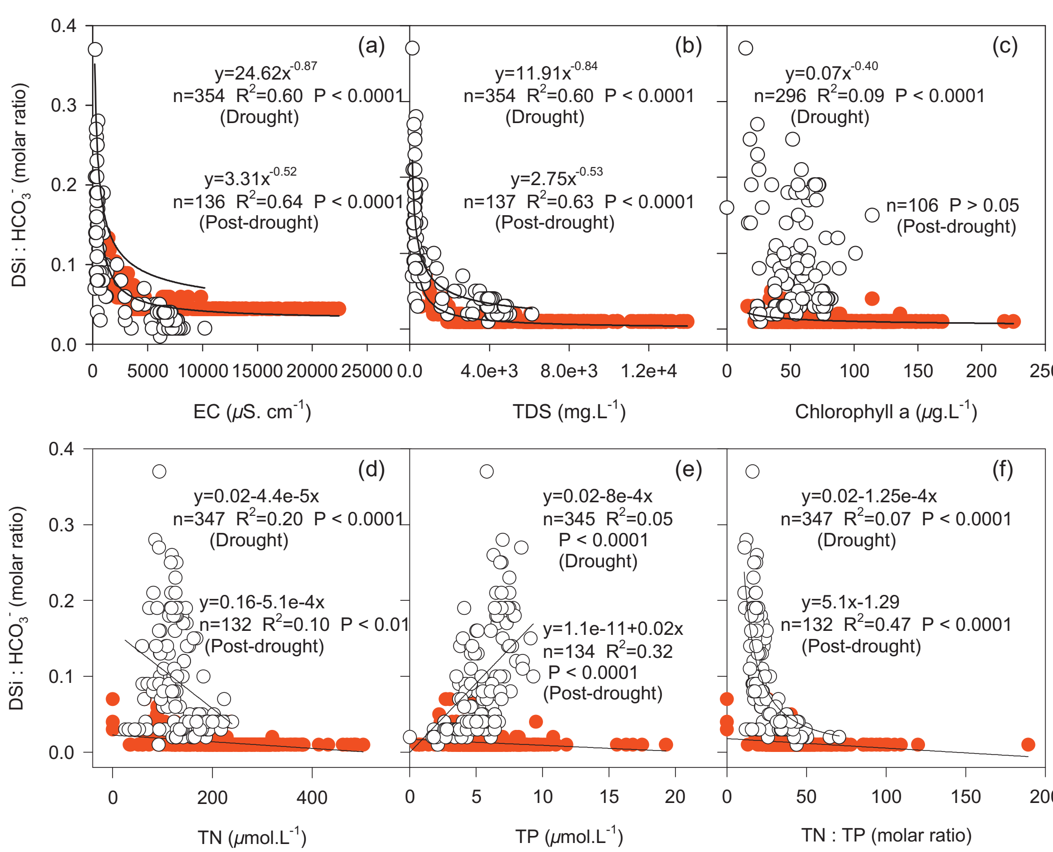

Fig. 3. Plots of DSi:HCO_3^- versus EC (a), TDS (b), chlorophyll *a* (c), TN (d), TP (e) and TN:TP (f) during the drought and post-drought period in the Lower Lakes, respectively.

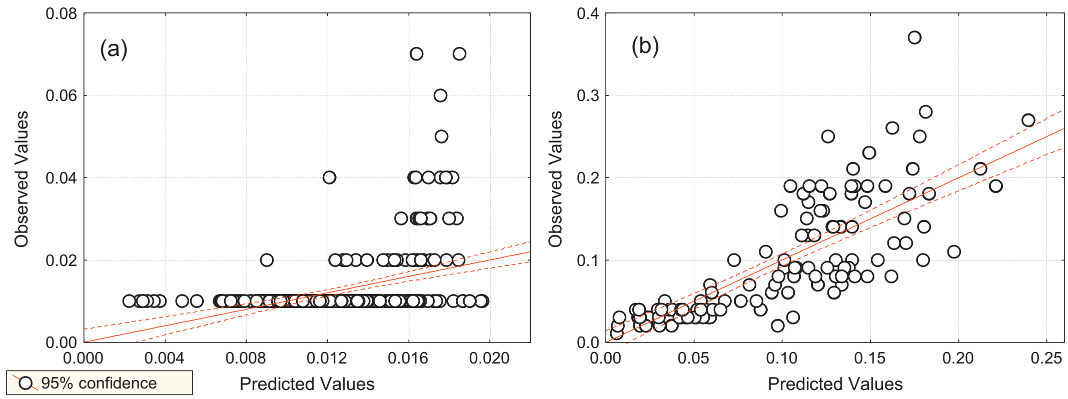

Fig. 4. Scatterplot correlations between predicted and observed values using BSRA for dependent variable DSi:HCO_3^- in the period of drought (a) and post-drought (b) in the Lower Lakes.

of the river inflows to the lakes and increase in the residual time that is pertaining to evapo-concentration (Olds et al., 2011; Mosley et al., 2012). This is supported by the significant inverse relationships between water level and determinants in the drought period (Table S1). The DSi and DIN concentrations decreased notably during drought (Table 1). This can be attributed to the diatom activities and denitrification in the lake system (Gibson et al., 2000; Cook et al., 2010). The significantly positive correlations between Chl-*a* and HCO_3^-, TN and TP respectively, and significantly negative correlation with DSi in the drought indicated active phytoplankton development, and consequent sequestration of C and silicon (Si) by diatoms in the Lower Lakes (Cook et al., 2010; Wang et al., 2016). Meanwhile, the atmospheric deposition and anthropogenic sources could replenish C, N and P, but not Si in the Lower Lakes (Jassby et al., 1994; Elser et al., 2009; Cook et al., 2010), leading to decreased DSi and contrasting increases of HCO_3^-, TN and TP in the drought period (Table 1). The flushing recharge at the break of drought could provide nutrients for the lakes in the post-drought period, increasing DSi concentration while diluting some other constituents (Table 1) (Mosley et al., 2012; Li et al., 2017).

The lower stoichiometric DSi:Na^+ and HCO_3^-:Na^+ during drought may be due to the inverse trends between DSi and HCO_3^- and Na^+ (Table S1). Na-normalized concentrations can minimize the heterogeneity originated from external influences (e.g. land cover, runoff and evaporation) (Meybeck, 2003) in the MDB, as weathering processes are typically the key contributor to Na^+ (Négrel et al., 1993) for the Lower Lake complex. Therefore, the significantly positive power correlations between Na-normalized DSi and HCO_3^- (Table S1, Fig. 2) reflected the intensive chemical weathering in the MDB (Wang et al., 2016). Further, the dominant determinants of DSi, HCO_3^-, Na^+ and EC in the Lower Lakes also demonstrated the leading role of chemical weathering (Table 2). However, the anthropogenic sources of nutrients also played pivotal loadings in the Lower Lakes (Table 2), mainly because broad-scale dryland and irrigated agriculture are a major land-use in the lower regions of the MDB. Sewage discharge and non-point pollution are also known potential sources of nutrients in the study region (Mosley and Fleming, 2010).

Table 2
Coefficients and variations (%) of the silicon, carbon and selected indices in the Lower Lakes.

Variable	Drought			Post-drought		
	Component			Component		
	1	2	3	1	2	3
DSi	**−0.785**	0.36	0.17	*−0.59*	*0.651*	0.054
HCO_3^-	**0.827**	0.311	0.289	**0.924**	0.308	−0.007
Na^+	**0.914**	0.343	0.08	**0.979**	0.067	0.012
DSi:Na^+	**−0.903**	0.325	0.063	**−0.89**	0.029	0.197
HCO_3^-:Na^+	**−0.941**	0.012	0.069	**−0.922**	−0.043	0.103
DSi:HCO_3^-	**−0.885**	0.246	0.012	**−0.956**	0.086	0.128
EC	**0.916**	0.357	0.065	**0.976**	0.101	0.001
pH	0.214	−0.476	*−0.598*	**0.793**	0.068	−0.29
Chl-*a*	0.253	−0.418	*0.724*	0.145	**0.922**	−0.212
Water level	*−0.588*	*0.578*	0.136	0.104	0.211	*0.736*
DIN	−0.465	*0.564*	0.454	0.204	−0.248	*0.607*
TDS	**0.907**	0.362	0.091	**0.977**	0.095	−0.006
TN	**0.858**	0.018	0.249	0.354	**0.797**	0.341
TP	0.067	*−0.706*	0.6	−0.521	**0.786**	−0.032
TN:TP	*0.742*	*0.565*	−0.277	*0.712*	−0.169	0.487
Eigenvalue	8.244	2.641	1.745	8.229	2.795	1.462
% of variance	54.96	17.61	11.63	54.86	18.63	9.75
Cumulative %	54.96	72.57	84.20	54.86	73.49	83.24

Bold and italic values represent the strong (>0.75) and moderate (0.75–0.5) loadings, respectively (Liu et al., 2003).

The average DSi:HCO_3^- ratio in drought period was lower than post-drought (Table 1). This may be attributed to the different supplies of nutrients in the distinct periods. The dominant chemical weathering contributed abundant nutrient materials to the Lower Lakes, but this was limited in the drought period due to much low water flows, and was enhanced in the post-drought period as a consequence of flow recharge. The algal activities could significantly regulated the DSi:HCO_3^- ratio in Lower Lakes, which was supported by the different relationships between DSi:HCO_3^- and Chl-*a*. The DSi:HCO_3^- ratio had significantly negative relationships with Chl-*a* in the drought period, but not in the post-drought period (Table S1, Fig. 3). This was in great agreement with Wang et al. (2016), who suggested that lacustrine DSi:HCO_3^- ratio should not reflect the characteristics of chemical weathering determined by the catchment, because the algal activities differentially utilise Si over C, as shown by inverse correlations with Chl-*a*.

The DSi:HCO_3^- ratio showed the distinct relationships with TP, TN:TP, while had the similar negative correlations with EC, TDS and TN in drought and post-drought period (Fig. 3). TN, TP and TN:TP partly indicated the development of phytoplankton and thus was reasonably correlated with DSi:HCO_3^- ratio. The EC reflected the water quality and TDS indicated the rate of the silicate chemical weathering of the catchment, which the similarly negative correlation between DSi:HCO_3^- and TDS was found by Wang et al. (2016). Importantly, and directly within the aim of this study, the BSRA was used to eliminate the multicollinearity among variables, and the result showed that drought may decouple the geochemical linkages of Si and C and their correlations with other water constituents in the Lower Lakes. TN appeared to be the best predictor for stoichiometric DSi:HCO_3^- in the drought period, and pH, TN and TP were the predictors in the post-drought period (Table S2, Fig. 4). This may be attributed to the efficient contribution of nutrients (e.g. TN and TP) to the development of diatom in the Lower Lakes. However, interpretation of the much lower DSi:HCO_3^- ratio in the drought period further demonstrates the magnitude of drought-related decoupling of silicon and carbon geochemical linkages, also reflected by the marginal correlations between stoichiometric DSi:HCO_3^- and other determinants in the Lower Lakes.

Droughts are increasing in frequency and severity around the world due to the anthropogenic activity and climate change. As the long-term water over allocation and timely rainfall reductions, the Lower Lakes experienced a millennium drought that induced the intense deterioration of water quality and marked shifts of lake biogeochemical cycles (Aldridge et al., 2011; Mosley et al., 2012; Li et al., 2016). The linkages between DSi and HCO_3^- originated from catchment chemical weathering, but commonly modified by the algal activity in lakes (Wang et al., 2016), whereas the drought condition in the Lower Lakes significantly aggravated the unbalance of silicon and carbon coupled because of the average lower DSi:HCO_3^- ratio (averaged 0.01) in drought period than American lakes (0.06) (Wang et al., 2016), the English Lakes (0.12) (Wang et al., 2016) and that in marine diatoms (0.13) (Brzezinski, 1985), and freshwater diatoms (0.79) (Sicko-Goad et al., 1984). The post-drought recovery to some extent significantly increased the DSi:HCO_3^- ratio (averaged 0.09) and repaired the linkages between stoichiometric DSi:HCO_3^- and other water quality indices in the Lower Lakes. However, the silicon and carbon coupled processes and linkages with other water constituents may be requires to be tested with a prolonged water quality monitoring in the Lower Lakes and also more widely data in other regions.

5. Conclusions

Stoichiometric DSi:HCO_3^-, DSi:Na^+ and HCO_3^-:Na^+ were dramatically lower in drought period in comparison to those in the post-drought period. DSi:Na^+ was significantly correlated with HCO_3^-:Na^+ in both drought and post-drought period. Chemical weathering supplied the main materials for the Lower Lakes, and anthropogenic activities also aggravated potentially water ecosystem. DSi:HCO_3^- ratio had almost relatively weaker correlations with other water constituents in the drought period than those in the post-drought period. The DSi:HCO_3^- ratio could be predicted by TN in drought period, but better by pH, TN and TP in the post-drought period considering the multicollinearity. Overall, drought decoupled the silicon and carbon geochemical linkages and those with other water constituents in the Lower Lakes. Our results further highlight the magnitude of impacts of extreme drought on silicon and carbon geochemical linkages, providing a new perspective on water quality management for lakes and those aquatic ecosystems following the increasing drought events due to anthropogenic activities and climate change in the future.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.04.074.

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